ON THE RELATIONS EXISTING BETWEEN CARBAZOL AND PYRROL.

BY SAMUEL C. HOOKER, Ph. D.

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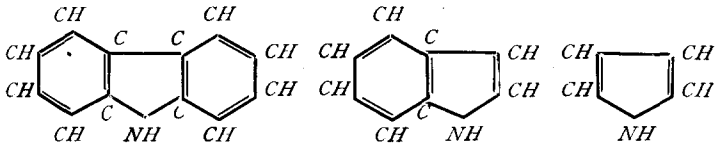
The theoretical relation existing between carbazol, indol and pyrrol is well shown by comparing their formulæ as follows:



The analogy existing between indol and pyrrol has received important experimental demonstration from the researches of v. Baeyer, E. Fischer,* and Ciamician,† but up to the present time no material evidence has been accumulated to show that a similar relation exists between carbazol and pyrrol. The formation of carbazol from thio-diphenylamine‡ by the action of copper furnishes some proof in support of the formula given above; but as this is the only reaction clearly tending to show that carbazol is a di-ortho derivative of diphenyl, and, therefore, that it contains the pyrrol ring, further evidence in the same direction appears desirable.

In making the experiments which led up to the facts here recorded, I hoped to find points of resemblance between carbazol and pyrrol for which the >NH group alone, independent of the pyrrol ring, would not account, and thus to confirm indirectly the above formula of carbazol.

Runge, the discoverer of pyrrol, observed that its vapor in contact with pine moistened with hydrochloric acid,

* *Ber. d. chem. Ges.*, **19**, 2,988.

† *Ibid.*, **19**, 3,028.

‡ *Ibid.*, **20**, 232.

colored the wood intensely red. Von Baeyer subsequently described this reaction as being very characteristic of indol. It is interesting, therefore, to find that carbazol reacts similarly, though not so readily. In order to observe the reaction, soak the wood—an ordinary match-stem answers admirably—for a second or two in a hot alcoholic or acetic-acid solution of carbazol, and then thrust it into the neck of a bottle containing concentrated hydrochloric acid, so as thoroughly to expose it to the action of the gas without bringing it in contact with the acid solution. The red color soon develops, and slowly increases in intensity. The shade is precisely similar to that produced by pyrrol.

Since carbazol may be regarded as a derivative of indol in which the two carbon atoms of the indol ring are connected with the group C_4H_4'', this observation appears directly to contradict one of the deductions made by Emil Fischer* in the course of his study of indol derivatives. "The fir-wood reaction," he says, "no longer occurs when both the carbon atoms of the indol ring are connected with alkyls."

It seemed necessary, therefore, to confirm my results by substituting synthetical carbazol for that extracted from coal tar, with which I first obtained the reaction. In spite of careful purification, it is conceivable that the coal-tar carbazol might still retain traces of foreign substances capable of imparting to it the power of coloring the wood.

Through the kindness of Dr. A. Goske in forwarding to me a sample of carbazol recently obtained by him† by the action of copper on thio-diphenylamine, I have been able to confirm the results of previous experiments in a satisfactory manner.

It seems possible therefore that the di-alkyl derivatives of indol which do not, according to Emil Fischer, give the fir-wood reaction when the test is made in the usual way, may do so if the conditions of the experiment are somewhat varied.

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* *Ber. d. chem. Ges.*, **19**, 1,570.

† *Ibid.*, **20**, 232.

CARBAZOL AND ISATIN.

The behavior of thiophene (and furfuran) in forming coloring matters with isatin and ortho-diketones apparently similar to those of pyrrol, makes it probable that in such reactions the >NH group of pyrrol takes no part. Consequently, in the case of carbazol, as all the hydrogen atoms of the pyrrol ring, excepting that of the imide group, are already substituted, it is not to be expected that any similar coloring matters can be formed. For this reason I was surprised to find that the behavior of carbazol and isatin in the presence of sulphuric acid is such as to strongly suggest the indophenine reaction.

On adding concentrated sulphuric acid to carbazol and isatin, an intense blue color is developed as the substances dissolve. The reaction is extremely characteristic and can be used as a delicate test for the recognition of carbazol. The blue color of the solution does not appear to be affected by slightly warming, and even after standing some hours its intensity had not materially diminished or its color otherwise changed. Water precipitates an indigo-blue substance which very rapidly becomes lighter in color. In order to avoid this change, attempts were made to extract the blue coloring matter from the acid solution without the addition of water, by agitation with various solvents. These experiments proved unsuccessful, and the further study of the compound was abandoned.

Although the above is very like the indophenine reaction and its apparently analogous reaction in the case of pyrrol, I am inclined to believe, for considerations already mentioned, that the similarity is apparent only and not real. Diphenylamine gives no reaction with isatin under the same circumstances.

Since diphenylene-oxide and diphenylene-sulphide are probably related to furfuran and thiophene, respectively, in the same way as carbazol is to pyrrol, it seemed of importance to ascertain whether these substances also behaved similarly with isatin. I was unable to obtain any reaction with diphenylene-oxide, and consequently it is probable that diphenylene-sulphide also will be found indifferent.

CARBAZOL AND QUINONE.

The compounds produced from pyrrol and benzoquinone have no corresponding members in the thiophene series, and would appear to be directly or indirectly dependent upon the >NH group for their existence; it therefore seemed possible that carbazol and benzoquinone might react with the formation of similar compounds.

If a small quantity of sulphuric acid, diluted with one or two volumes of acetic acid, is added drop by drop to an acetic-acid solution of carbazol and benzoquinone, an intense carmine red solution is produced, which passes into a reddish-violet as the quantity of sulphuric acid is increased. Water precipitates from this solution a substance of the same color, which dissolves very readily in ether, chloroform and alcohol.

On the addition of crystals of quinone to carbazol dissolved in concentrated sulphuric acid, an intense green color is imparted to the solution. Hence, according to the strength of the acid used, a reddish-violet or a green solution is obtained.

Similarly Victor Meyer and O. Stadler * haves hown that benzoquinone reacts with pyrrol in two distinct ways. If aqueous solutions of the two are mixed, a violet coloring matter is produced, whereas in the presence of dilute sulphuric acid a green precipitate is formed. For purposes of comparison I repeated V. Meyer and Stadler's experiments. The violet coloring matter obtained dissolved in ether to a solution very similar in shade to that of the ethereal solution of the coloring matter from carbazol.

Before concluding that the formation of these compounds is in any way connected with the existence of the pyrrol ring, it seemed necessary to study the action of diphenylamine under similar circumstances. Sulphuric acid added to diphenylamine and quinone dissolved in acetic acid immediately colors the solution blue; on adding water, a violet substance is precipitated.

These reactions recall the coloring matters obtained by

* *Ber. d. chem. Ges.*, **17**, 1,035.

P. Greiff * by heating chloranil or quinone with methyldiphenylamine and other amines with or without the addition of zinc chloride. The similarity existing between the method of formation and the shade of Greiff's coloring matters and the violet compounds obtained as above described from pyrrol, carbazol and diphenylamine, renders it extremely probable that in both cases the coloring matters are perfectly analogous, and that their formation in the case of pyrrol and carbazol depends upon the amine character of these substances, and not upon the presence of the pyrrol ring. This view, which could not, unfortunately, be substantiated by analysis, owing to the great instability of the pyrrol compound, receives support from the fact already alluded to that thiophene gives no coloring matters with benzoquinone.

With reference to the green solution formed on adding quinone to carbazol dissolved in sulphuric acid, it seems probable that in this case quinone plays the part of an oxidizing agent only, for the same green-colored solution is produced, as is well known, by the addition of oxidizing agents generally under similar circumstances. It occurred to me, therefore, as not unlikely that quinone acts merely as an oxidizing agent also, when in contact with pyrrol in acid solution, especially as V. Meyer and Stadler extracted hydroquinone in considerable quantities from the mother-liquor after the green compound had been filtered off. Confirmation of this view was obtained by reference to Anderson's † description of the properties of pyrrol. He states that ferric chloride causes a dilute hydrochloric-acid solution of pyrrol to turn first *green* and then black. He adds that platinic chloride and potassic bichromate produce a black precipitate with the same solution.

A few experiments soon proved that not only ferric chloride, but potassic chromate or bichromate, platinic chloride, potassic ferricyanide, and even potassic nitrite under certain circumstances, all give, when added in small quantity

* *Ber. de chem. Ges.*, **12**, 1,610.

† *Ann. Chem.* (Liebig), **105**, 354.

to a dilute sulphuric-acid solution of pyrrol, a green substance which passes more or less rapidly, according to the oxidizing agent used and the acidity and degrees of concentration of the solutions employed, into the black compound observed by Anderson. With tolerably concentrated solutions of the oxidizing agents, the transition is so rapid that the green color can be scarcely observed, even when the sharpest lookout for it is maintained throughout the experiment.

With a dilute solution of potassic chromate, the formation of the green substance may be readily seen, and the reaction compared with that of quinone. As it is not easy, however, to obtain the reaction at its best without a number of trials, I prefer to give the exact strength of the solutions which I found to give good results. Eight drops of pyrrol are dissolved in 10 cc. of water to which eight drops of sulphuric acid have been added. When this is mixed with an 0·1 per cent. solution of potassic chromate in equal volumes, the green color is almost immediately developed, and rapidly increases in intensity until the solution becomes perfectly opaque. At this stage three or four volumes of water are added. The diluted solution is green in color, and slowly deposits a dark green or black precipitate.

A very dilute aqueous solution of quinone behaves almost precisely similarly with the above solution of pyrrol, but the precipitate formed is at first much greener than when potassic chromate is the oxidizing agent used. It gradually darkens, however, and after some hours becomes almost black. If the green precipitate from quinone is washed with an 0·05 per cent. solution of potassic chromate, it is very rapidly blackened.

From these experiments it would appear extremely probable, therefore, that quinone does not condense with pyrrol in acid solution, but merely acts like other oxidizing agents.

The formation of green substances like the above is not confined to the action of oxidizing agents on carbazol and pyrrol. It has long been known that nitrous acid and other oxidizing agents added in small quantity to diphenylamine

dissolved in sulphuric acid, produce an intense blue solution from which water precipitates a green compound; this, like the corresponding compounds from carbazol and pyrrol, is insoluble in ether.

PYRROL AND PICRIC ACID.

The behavior of indol and carbazol in combining with picric acid suggested the idea that probably pyrrol would form a similar compound. On adding picric acid to an excess of pyrrol, a red color is at once developed; on warming, the picric acid is dissolved, and the solution, when cold, deposits beautiful red needles. Similarly, if picric acid and an excess of pyrrol are dissolved in alcohol, long red needles, half or three-quarters of an inch in length, can be readily obtained as the solution is allowed to evaporate. The compound is very unstable, and commences to decompose in the air as soon as the crystals are dry. Its fusing point is about 71°. Since the basic properties of pyrrol are very weak, and no well-defined salts have been obtained with acids generally, the above described compound must be considered as analogous to the picric acid compounds of the hydrocarbons. The relation of pyrrol to benzol, so often dwelt upon by Victor Meyer, is thus once again emphasized. Phenyl-pyrrol also forms an unstable compound with picric acid. The compounds of pyrrol and its derivatives with picric acid will be further studied, and an attempt will be made to analyze them.

[COMMUNICATION.]

FOR SEALING OF VOLATILE LIQUIDS IN GLASS TUBES.

GENTLEMEN: The following communication on "The Sealing of Volatile Liquids in Glass Tubes," may be found of general interest. In order that glass tubes containing very volatile liquids may be properly sealed, the temperature of the tubes and their contents must be so lowered that the vapor tension of the liquid is not greater than the